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Study of crystal formation in titanate glass irradiated by 800 nm femtosecond laser pulse

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Abstract

The structure of the titanate glass is destroyed during irradiation by the femtosecond laser pulses, and $(TiO_6)^{8-}$ and $(TiO_4)^{4-}$ anion units are exsolved from the network of the titanate glass. These anion units are rearranged to form some crystals such as anatase and Ba_2TiO_4 crystals. By Raman spectroscopy, it is found that these crystals have a strong dependence on the intensity of the femtosecond laser pulses. The relation between the generation of these crystals and space distribution of the femtosecond laser power intensity is qualitatively explained.

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Keywords: A1. Anatase crystal; A1. Femtosecond laser; B1. Titanate glass; B3. Raman spectra

1. Introduction

Because of its ultrashort interaction time and high peak power, the femtosecond laser is able to induce nonlinear optical effects in glasses. These effects include multiphoton absorption and multiphoton ionization [1,2]. The femtosecond laser has been used for micromodification of transparent dielectric materials to produce functional microstructures with various applications [3–5].

It is well known that glass is in a metastable state with an inherent tendency to change into a more stable state. Because the temperature for glass transition and crystallization is rather low, the high temperature (the temperature 100 μm below the surface of the sample is about 10^6 K) and strong internal pressure fields created by a femtosecond laser pulse should be sufficient to

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rearrange structures and produce crystals in metastable glass.

In this paper, we demonstrate the ability of femtosecond laser irradiation to form crystals in focal areas in glass samples. Such structural modifications have been verified by Raman spectroscopy. Therefore, it is feasible to apply femtosecond laser technology in the fabrication of integrated optical devices.

2. Experiment

The composition of the titanate glass studied was $32.5BaO–32.5TiO_2–35SiO_2$(mol%). Reagent-Grade $BaCO_3$, TiO_2 and SiO_2 were used as starting materials. A mixed batch was melted in a Pt crucible at 1250 °C for approximately 2 h. Then the Pt crucible was put into cold water to prevent the crystallization of the glass. The glass obtained was then cut and polished. The samples were all polished and cut into 5 mm × 5 mm × 2 mm–sized pieces.

The femtosecond laser system consisted of three main parts, which included a femtosecond laser source, a beam focusing system, and a three-dimensional movable platform (see Fig. 1).

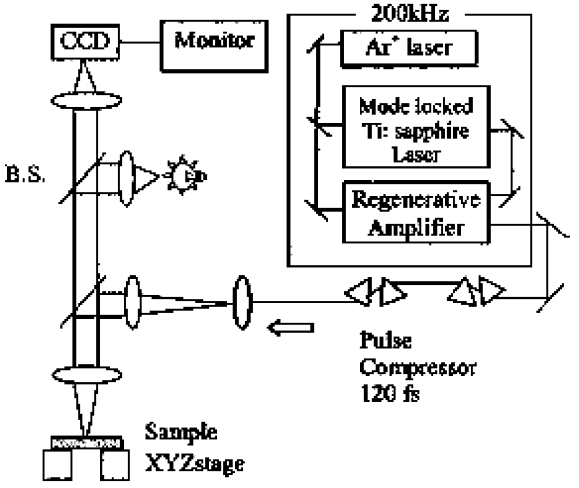

Fig. 1. Femtosecond laser system: B. S., beam splitter.

The irradiation source was a regenerative amplified 800 nm Ti:sapphire laser that emits mode-locked light with a pulse duration of 120 fs and a repetition rate of 200 kHz, and the energy of single pulse is 420 mJ.

A microscope with a 5× objective lens and a numerical aperture of 0.8 was used to focus the laser beam to a spot size of approximately 10 μm. The laser beam was focused onto a plane 100 μm below the surface of the sample.

It is essential to control the laser's intensity to avoid damaging the glass onto which the laser is focused. In this experiment, we set the fluence of the laser irradiation at $4.0 \times 10^{12}\,W\,cm^{-2}$and the repetition rate of the pulse at 200 kHz.

The Raman scattering experiment was performed with a SPEX 1877 Raman spectrometer and Olympus BX41 confocal microscope. The excitation light source was an Ar ion laser with a wavelength of 514.5 nm and a power of 4 mW. A 50× objective lens was used to focus the beam onto the sample. The grating of spectrometer has 1800 lines mm^{-1}. The spectrum's scattering detection region ranges from 30 to 1400 cm^{-1} with a 300 s exposure time and CCD detector. The scattered radiation was measured at an angle of 180° from the incident laser beam.

3. Results and discussions

The generation of crystals in titanate glasses that have been irradiated by femtosecond infrared laser pulses was examined by Raman spectroscopy. Significant structural changes were detected in the focal area at a plane of 100 μm below the surface. The glass sample was irradiated for 20 min. The sample irradiated by femtosecond laser pulse was shown in Fig. 2. We select one irradiated point to study the change of the microstructure. The point at which the green arrow directs is the measurement point. The point's diameter is about 40 μm.

Fig. 3. illustrates the Raman spectrum of titanate glass, which is irradiated by 800 nm femtosecond pulses for 20 min.

ABCDEFG in Fig. 3 corresponds with different locations above, on, and below the measurement point in Fig. 4.

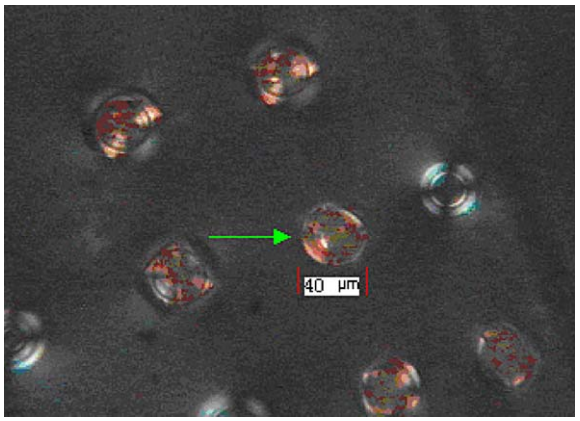

Fig. 2. Titanate glass sample irradiated for 20 min under cross-polarized light.

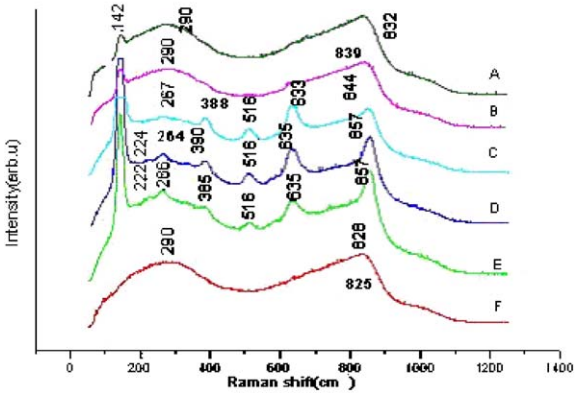

Fig. 3. Raman spectrum of titanate glass irradiated for 20 min.

In Fig. 3A, the strong peak at 832 cm^{-1} can be assigned to the stretching vibration of the Ti–O bond in the TiO_4 [6] unit. A weak band from 680 to 700 cm^{-1} is the stretching vibration of the Ti–O bond in the octahedral TiO_6 unit. The bending vibration of the Ti–O bond in the TiO_4 unit is shown at 290 cm^{-1} when the upper surface of the sample was irradiated by the femtosecond laser pulse for 20 min, a new peak at 142 cm^{-1} would appear; however, the peaks at 832,290 cm^{-1} still remained there. It was shown that the structure of the glass was modified a little.

In curve B of Fig. 3, the band at 142 cm^{-1} becomes narrower than that in curve A. The peaks between 680 and 700 cm^{-1} change into some peaks

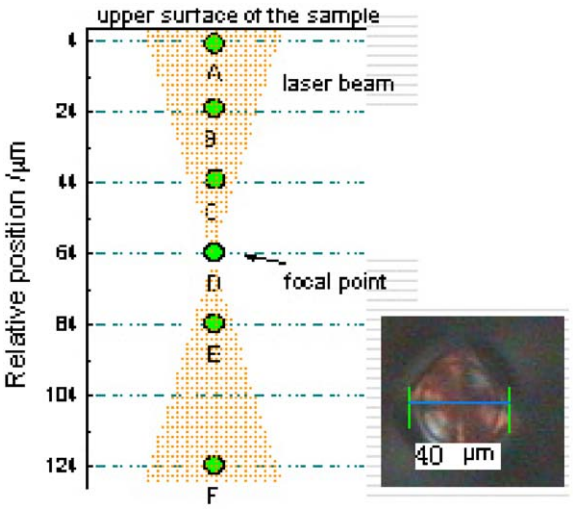

Fig. 4. Locations of Raman detection in the sample.

between 600 and 650 cm^{-1} and 832 cm^{-1} peak shifts to 839 cm^{-1}.

It is shown in curve C of Fig. 3 that C point possesses characteristic bands at ~267, 388, 516, 633, 844 cm^{-1}. In comparison with curve B, 290 and 839 cm^{-1}shift to 267 and 844 cm^{-1}, respectively. Peaks at 142, 388, 516, 633 cm^{-1} are consistent with anatase Raman spectrum in Ref. [7]. The vibration mode symmetries of the anatase are [8] as follows: A_{1g} – 513 cm^{-1} B_{1g} – 388 cm^{-1}, E_g – 633, 142 cm^{-1}. The intensity at 142 cm^{-1} is very high, while 267 and 844 cm^{-1} are similar to Ba_2TiO_4 crystal's Raman characteristic spectrum. It is derived that anatase and Ba_2TiO_4 crystal have been induced in C point of the sample.

In curve D of Fig. 3, the peak at 844 cm^{-1} shifts to 857 cm^{-1} which indicates the formation of Ba_2TiO_4 crystal [9]. The fingerprint peaks ascribed to anatase and Ba_2TiO_4 crystal are very clear so that we can draw a conclusion that anatase and Ba_2TiO_4 crystals coexist in point D.

Curve E is very similar to curve C.

Ba_2TiO_4 is one of the few compounds containing tetrahedrally coordinated titanium. Its space group is $p2_1/n$, C_{2h}^5 [10]. All atoms are, in general, positions with a 4-fold multiplicity so that there is only one kind of titanium and two different sites for the barium atoms. The TiO_4 tetrahedra are isolated and are slightly distorted with one Ti–O(1)

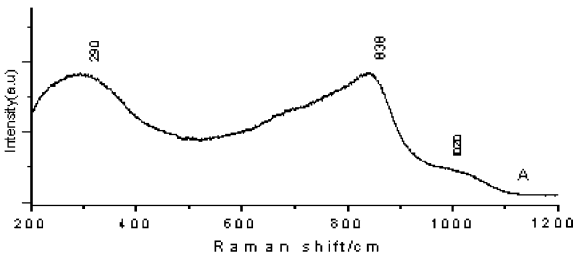

Fig. 5. Raman spectra of titanate glass unirradiated.

bond significantly shorter (1.766 Å) than the other three bonds (mean value: 1.822 Å). This distortion results from the fact that O(1) is coordinated to only three Ba atoms while each of the other O atoms are bonded to four Ba atoms [11].

Curve F is the same as that of unirradiated glass, which indicates that the construction of point F is not modified. Fig. 5 shows the Raman spectrum of unirradiated glass.

Fig. 5 illustrates the Raman spectrum of titanate glass ($32.5BaO–32.5TiO_2–35SiO_2$(mol%)). The peak at $1020\,cm^{-1}$ is attributed to the asymmetrical stretching vibration of the Si–O–Si bond in the SiO_4 unit [12]. The strong peaks at $838\,cm^{-1}$ can be assigned to the stretching vibration of the Ti–O bond in the TiO_4 [6] unit. A weak band from 680 to $700\,cm^{-1}$ is the stretching vibration of the Ti–O bond in the octahedral TiO_6 unit. The bending vibration of the Ti–O bond in the TiO_4 unit is shown at $290\,cm^{-1}$. The Raman spectrum indicates that this glass is composed of quadridentate or sexidentate Ti, including TiO_4 tetrahedra, SiO_4 tetrahedra, and TiO_6 octahedra.

In general, titanium oxide contains TiO_4 tetrahedra and TiO_6 octahedra [13–15]. The formation of TiO_4 tetrahedra and TiO_6 octahedra is related to the number of nonbridging oxygen and the ability to capture free oxygen [16,17].

Point D is the focus point, where the intensity of the femtosecond pulses is very high. So the titanate glass is completely melted and the chemical bond of the titante glass is broken. $(TiO_6)^{8-}$ and $(TiO_4)^{4-}$ anion units are exsolved from the network of the titanate glass and rearrange to form their corresponding crystals. $(TiO_6)^{8-}$ anion units to generate anatase crystals and $(TiO_4)^{4-}$ anion units and Ba^{2+} are incorporated into Ba_2TiO_4 crystal. These two crystals can coexist at point D.

4. Conclusions

1. In general, when the intensity of the laser pulses increases, the quality of the anatase and monocrystalline Ba_2TiO_4 becomes more perfect and the quantity of anatase becomes much bigger. It is shown that the generation of these two crystals in the titanate glass has an intimate relation with the distribution of intensity of laser pulses.
2. In titanate glass, $(TiO_6)^{8-}$ and $(TiO_4)^{4-}$ anions units are incorporated into the network and are exsolved by the heat effect of the femtosecond laser pulse. These anions then form these two crystals. A conclusion can be drawn that the generation of these two crystals are very close to the structure of the titanate glass.
3. Fig. 3 shows the Raman spectra obtained from several layers of glass by focusing of the Raman probe laser beam above, on, and below the femtosecond laser's focal area that had been irradiated for 20 min. Fewer weaker peaks are seen in spectra A, B, C, E, F than in spectrum D, which indicate that crystallization decreases with increasing distance from the focal point. It illustrates again that the generation of these two crystals is dependent on the space distribution of the femtosecond laser power intensity.

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